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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

APPLICANT(S): John R. Saffell et al.

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LETTER REGARDING SUBMISSION OF PRIORITY DOCUMENT

The above referenced application claims priority from Great Britain patent application GB 0027877.0, filed November 15, 2000. Applicant submits herewith a certified copy of the priority application.

Respectfully submitted,

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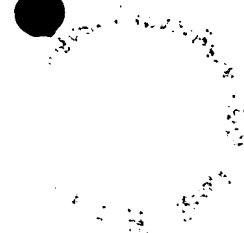
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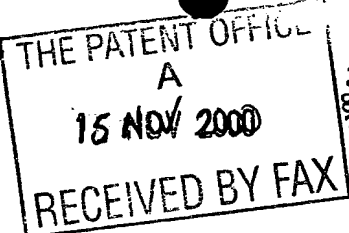
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Andrew Gersay

Dated 19 NOV 2001



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1. Your reference

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2. Patent application number

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0027877.0

15 NOV 2000

3. Full name, address and postcode of the or of each applicant (underline all surnames)

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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UK

7518863001

IS

4. Title of the invention

Electrochemical gas sensor

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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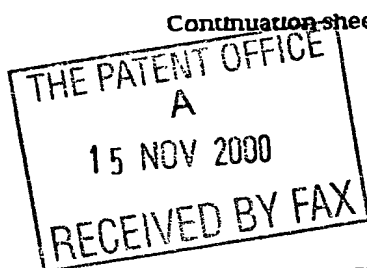
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12 ✓

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11.

I/We request the grant of a patent on the basis of this application.

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Neil McRechnie
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ELECTROCHEMICAL GAS SENSOR

The present invention relates to the field of electrochemical gas sensors. In particular it relates to electrochemical gas or vapour sensors where, as well as the target gas, a reagent gas needs also to be supplied to or removed from the counter electrode. In these sensors, the target gas or vapour reacts at one electrode of the electrochemical cell and the current generated by this electrochemical reaction is balanced by a reaction at a counter electrode with an intervening body of electrolyte. This electrochemical cell may also include a third reference electrode which sets a characteristic potential of the electrochemical cell to assist in regulating the electrochemical reaction at two electrodes. Primary applications are to the detection of toxic or other gases in the atmosphere and the most preferred application will be for detection of carbon monoxide in air, where it is important that oxygen is supplied to the counter electrode.

BACKGROUND TO THE INVENTION

In recent years the need for detecting and measuring toxic, noxious and irritating gases in the environment has increased as public awareness of the potential dangers and corporate awareness of potential accidents and death by gas poisoning has increased.

Numerous sensing systems have been developed to measure these gaseous components. Although direct chemical methods exist, other analytical techniques such as gas chromatography, infrared absorption and molecular fluorescence have all been used to quantify toxic or noxious gas concentrations in the atmosphere.

However, chemical methods of gas detection continue to dominate. These chemical methods depend on either a property change to a sensing material, such as conductivity, dielectric constant, mass change or semiconductor behaviour have all been used to monitor toxic gas concentration either qualitatively or quantitatively. Colourimetric detection tubes (see K Grosskop "Angew.Chemie", vol 63, pages 306 - 308, 1962) have been used for several decades. However, the above techniques suffer from either lack of discrimination of the gas species or from excessive power demands for solid state semiconductor devices which must operate at typically 500°C.

The most popular gas detection method is wet electrochemistry whereby the target gas reacts electrochemically with the working electrode of the electrochemical gas sensor. The result of the reaction at this working electrode can be either measured as a voltage change (potentiometry) or as a current generated by the reaction (amperometry). The present invention is concerned with amperometric electrochemical cells for use as gas sensors.

In electrochemical gas sensors the target gas or vapour reacts at the working electrode of the electrochemical cell and the current generated by this electrochemical reaction is balanced by a reaction at the counter electrode. The electrochemical cell must be part of a complete electrical circuit so that the current generated at the working electrode must be conducted away from the cell to a circuit to measure this current. In addition this electrochemical cell will usually include a third reference electrode which sets a characteristic potential of the electrochemical cell, to regulate the electrochemical reaction at the working electrode. An external potentiostat circuit measures the reference electrode potential and supplies adequate current into the counter electrode, forcing a reaction at the counter electrode to balance the working electrode reaction. The potentiostat circuit not only provides the current required for the counter electrode but also ensures that the working electrode is operating at the same potential as the reference electrode, or if a bias voltage is inserted, then at a controlled bias relative to the reference electrode.

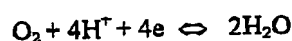
Like the working electrode, the counter and reference electrodes both require conductors to either allow electrical monitoring of the reference electrode potential or to complete the electric circuit to the counter electrode. At the counter electrode an opposite reaction to the working electrode, i.e. if the working electrode is oxidising a gas then the counter electrode will be reducing another species) will generate a by-product which may be either an ion or a gas. The creation or consumption of chemical components at both the working and counter electrodes requires that these required or resultant components are transported either to or away from the surface, so an effective electrolyte for rapid ionic transport is desirable.

One major concern with electrochemical amperometric gas sensors is ensuring that the electrolyte maintains continuous contact with the electrodes and between the electrodes. This has been done by changing the state of the electrolyte, alternative forms include electrolyte gels and solid state ion conductive membranes. However, the most popular method for transporting electrolyte within electrochemical cells including fuel cells, batteries and gas sensors is the use of a filler material which immobilises the electrolyte on to the surface of the filler material. The most popular geometry for filler material is fibres with glass fibre and asbestos traditionally serving these roles. Examples of this technology can be found as early as Billiter who used an asbestos matrix for ionic control in chlorine generating plants in the 1920's. More recently Binder in US patent no 4,036,724 has taught the use of asbestos fibres or aluminium oxide powder to immobilise electrolytes such as perchloric, sulphuric or phosphoric acid. Shaw in US patent 3,755,125 extended this knowledge to include the use of planar separator disks made from glass fibre with a wick extension that dipped into a liquid reservoir. This allowed continuous electrolyte access by the use of separator disks between the electrodes. Separator disks touched at the periphery of their surfaces to allow vertical wicking and four wick extensions into the reservoir allowed excess material to replenish evaporated electrolyte or excess electrolyte in high humidity applications to be stored in the reservoir. Chan et al. (GB patent no 2 094 005) tried to simplify the wicking method, since Shaw used four planar separators, with each displaced 90° relative to the next. Chan et al. employed a hole in the electrode with a single annular wick: a simpler design with the added advantage

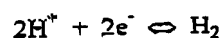
1 that the wick connecting the reservoir to the working electrode was continuous and did not require pressure between
2 the planar separators to ensure good contact for vertical capillary transport. However, both of these solutions have an
3 excessive number of hydrophilic components to allow adequate electrolyte transport and the single wick in the Chan
4 design is difficult to manufacture and wasteful of electrode material. Therefore, it would be useful to provide an
5 alternative low component cost method for transporting electrolyte within an electrochemical gas sensor.

6
7 Another problem considered in the design of electrochemical gas cells is not only the reaction at the working
8 electrode but the opposite reaction at the counter electrode and the stabilising reaction at the reference electrode.

9
10 The reaction at the reference electrode must be stable with time but does not require generation of a significant
11 current. Therefore the reference electrode can be small and the reaction rates can be slow, so long as the potential
12 resulting from the various reactions is constant. Therefore the reference electrode does not require a large flux of
13 chemicals to create an electrochemically stable environment. The counter electrode, however, must produce a current
14 equal and opposite in sign to the current created by the working electrode. The use of a potentiostatic circuit helps
15 since a potentiostatic circuit is designed specifically to maintain the working electrode at a fixed potential and allow
16 the counter electrode to vary its potential until it finds an electrochemically active species to reduce or oxidise. The
17 most common reaction is oxygen reduction but an alternative reaction is hydrogen gas generation. These two
18 reactions are shown below.



$$E^0 = 1.227\text{V}$$



$$E^0 = 0.0\text{V}$$

23
24 An electrochemical gas cell will be limited by either the gas access to and the activity of the working electrode or the
25 ability of the counter electrode to generate an equivalent balancing current. The first problem is not part of the
26 present invention and has been discussed elsewhere; design of catalytic systems for the working electrodes to
27 respond to specific gases is well known in the art. However the problem of providing adequate oxygen at the counter
28 electrode has received less attention and is commonly solved by three known methods.

29
30 Firstly, a counter electrode can be placed below the working electrode with intervening electrolyte whether it is gel,
31 solid or liquid immobilised in a fibrous matrix. The oxygen penetrates through the working electrode, then dissolves
32 into the electrolyte and is transported across the electrolyte to the counter electrode. This method of supplying
33 oxygen to the counter electrode is inherent in the design of nearly every electrochemical gas sensor design but will
34 limit the amount of oxygen accessible to the counter electrode by the thickness of the electrolyte layer, temperature
35 and type of electrolyte and the resultant oxygen solubility in the electrolyte and the rate of diffusion through the
36 electrolyte. Typically in a carbon monoxide sensor a 1 cm^2 counter electrode can generate about $300\text{ }\mu\text{A}$ of current
37 by oxygen reduction to balance the current generated by the working electrode. At higher current oxygen will be
38 reduced.

1 An alternative method is to allow the two electrodes to be a planar design with the working electrode having access to
2 the atmosphere under test and the back surface of the counter electrode having access to the same air. Oxygen would
3 then have direct access to the counter electrode in the same way as a working electrode. This symmetrical method
4 obviously needs an applied potential between the working and counter electrodes; otherwise the symmetry of the
5 system would disallow any chemical reaction. Therefore a three electrode system with a potentiostat circuit, driving
6 the working electrode to the same potential or to a bias potential relative to the reference will force this sensor to
7 operate correctly.

8
9 The introduction in the 1970s of commercially available gas porous hydrophobic electrodes such as Zitex® and
10 Goretex® has given electrochemical cell designers a new opportunity to design flexible gas porous hydrophobic
11 electrodes, providing a barrier to prevent the electrolyte from escaping but allowing access of oxygen and measured
12 gases to the catalyst/ binder composition which is laid onto the gas porous support. Coincidentally this also allows
13 radial diffusion of oxygen through the gas porous supports to the under-surface of the catalytic counter electrode
14 material. Solid PTFE or polypropylene supports can also be used, but the diffusion of gas through the solid
15 membranes is much slower and hence access to oxygen is much slower in a solid support than in a gas porous
16 support. Radial diffusion of oxygen to the counter electrode was taught by Tataria (US patent no 4,184,937). This
17 simple design was the first recorded use of radial gas diffusion using gas porous electrode supports for the counter
18 electrode. Chan et.al (GB patent 2 094 005) taught the use of access from the back of the sensor, around the reservoir
19 and then through the edges of the stack and radially into the counter electrode. This path is similar to the path as
20 defined by Tataria; however, the use of radial diffusion from the edge to the counter electrode has two problems:

21
22 Firstly, if the edge of the electrode stack assembly is enclosed within the sensor housing then channels from the
23 bottom of the sensor housing to the edges of the sensor must be created to allow oxygen access to the edge of the
24 counter electrode. This path can also be an electrolyte leak path so should be avoided in a good design.

25
26 Secondly, the sealing of the electrode by compression will also compress the electrode support. Increased
27 compression to ensure a more leakproof sensor will lead to reduced oxygen diffusion as the gas porous electrode is
28 compressed and the gas porosity decreases. Therefore it is not advantageous to depend on a route of oxygen flux
29 whose optimisation is contradictory to the sealing of a good gas sensor.

30
31 The present invention is directed at an efficient method of providing electrolyte to the electrodes of an
32 electrochemical amperometric gas sensor while also ensuring adequate oxygen supply to the counter electrode.

33
34 Other embodiments include the opportunity for supplying excess oxygen to the reference electrode, reducing the
35 effect of hydrogen gas on the reference electrode and increasing the oxygen access to the counter electrode. The
36 present invention is designed to be easy and cost effective to manufacture, robust, usable in any orientation and
37 leakproof, while providing easy access of oxygen of the counter electrode and reliable electrolyte transport to the
38 electrodes.

1 SUMMARY OF THE INVENTION

2
3 The present invention relates to electrochemical gas sensors, more particularly to gas sensors in which the target gas
4 or vapour reacts at one electrode of the electrochemical cell and the current generated by this electrochemical reaction
5 is balanced by a reaction at a counter electrode with an intervening body of electrolyte. This electrochemical cell may
6 also include a third reference electrode which sets a characteristic potential of the electrochemical cell to assist in
7 regulating the electrochemical reaction at two electrodes.

8
9 The present invention includes a compact electrochemical gas sensor in the form of electrochemical cell assembly
10 comprising a first planar working electrode comprising a planar hydrophobic gas porous support and the second
11 planar counter electrode comprising a planar hydrophobic gas porous support which contacts either directly or
12 indirectly the support of the working electrode with optionally a planar reference electrode interposed either in
13 between the two electrodes or beneath the counter electrode.

14
15 According to a first aspect of the present invention there is provided an electrochemical gas sensor for measurement
16 of a gaseous analyte, the sensor comprising a planar working electrode and a planar counter electrode with electrolyte
17 therebetween, the working electrode and the counter electrode being in contact with the electrolyte, the sensor further
18 comprising a gas diffusion means through which a reagent gas can diffuse to the counter electrode, the gas diffusion
19 means partially or fully enclosing a volume around the working and counter electrodes and having an electrolyte
20 supply means for supply of electrolyte from a reservoir, the counter electrode having an outer edge characterised in
21 that part of the outer edge of the counter electrode is in contact with the gas diffusion means and part of the outer edge
22 of the counter electrode is not in contact with the gas diffusion means, there being provided electrolyte transport
23 means for electrolyte to pass around the part of the outer edge of the counter electrode where it is not in contact with
24 the gas diffusion means.

25
26 The counter electrode may contact the gas diffusion means around the outer edge of the top surface and/or outer edge
27 of the bottom surface and/or outer face.

28
29 The gas diffusion means may comprise a hydrophobic gas porous support.

30
31 Preferably, the hydrophobic gas porous support is microporous PTFE.

32
33 Preferably, the gas diffusion means may comprise a plurality of separate parts in contact with each other.

34
35 Part of the gas diffusion means may be a support for the working electrode. Part of the gas diffusion means may be a
36 support for the counter electrode. The gas diffusion means may further comprise one or more washers. Preferably,
37 the largest dimension of the counter electrode is less than the inner diameter of the "O" ring seal.

38
39 Preferably, the electrolyte is supported by a wicking medium.

40

1 Preferably the working electrode and counter electrode are parallel to each other. The working electrode and counter
2 electrode may be coaxial.

3
4 The counter electrode may be a rectangle. Alternatively, the counter electrode may be a rectangle with rounded
5 corners or ends. Alternatively, the counter electrode may be a cross. Alternatively, the counter electrode may
6 comprise a circular central region with one or more arms extending outwards.

7
8 The counter electrode catalyst may face the reference electrode.

9
10 A reference electrode may be provided in contact with the electrolyte between the working electrode and counter
11 electrode.

12
13 The reference electrode and counter electrode may be formed from a single electrode cut into two parts. Preferably,
14 this will form two semi-circles. The semi-circles may not overlap. The reference electrode may be coplanar with the
15 counter electrode. The reference electrode may be formed on the same support as the counter electrode.

16
17 The reference electrode may comprise a non-gas permeable support, configured to reduce or eliminate diffusion of
18 hydrogen from the counter electrode to the reference electrode. The reference electrode support may have a hydrogen
19 removing means. The hydrogen removing means may be a metal or metal-organic layer. Typically, this will be
20 Palladium.

21
22 Preferably the gaseous analyte is carbon monoxide and the reagent gas is oxygen. Alternatively the analyte gas may
23 be hydrogen sulphide or sulphur dioxide.

24
25 The gas diffusion means may be enclosed in a non-porous medium having an aperture therein, the aperture being
26 positioned on the side of the working electrode away from the counter electrode.

27
28 Preferably, the non-porous medium has no apertures through which gas may penetrate to the gas diffusion means.

29
30 Optionally, there may be a small gap between the counter electrode and the gas diffusion means. Typically this will
31 be in the order of 0.5-1mm.

32
33 The accompanying drawings illustrate schematically the definitions used in the description of the preferred
34 embodiment, a detailed description of the preferred embodiment, and modifications for other embodiments.

35
36 Figure 1 is a plan view, labelling the dimensions of the example sealing O-ring, working electrode and a
37 hydrophilic separator disk;

38
39 Figure 2 is an exploded view of the preferred embodiment of the electrochemical gas sensor of the present
40 invention. Simple alternatives to the preferred embodiment are also shown;

Figure 3 is an exploded view of other embodiments of the present invention;

Figure 4 is a sectional view of the counter electrode 60, stack base 70 and working electrode 20, showing the possible oxygen transport routes;

Figure 5 shows a cross-section through an electrode stack in an embodiment having counter electrode 60; and

Figure 6 shows a cross-section through an electrode stack orthogonal to that in Figure 5.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in terms of the preferred embodiment shown in Figure 2.

Figure 1 labels the dimensions of an example electrode assembly stack of this electrochemical gas cell.

The construction of the preferred embodiment consists of a reservoir 90 supporting an electrode stack assembly 100 which is then sealed by an 'O' Ring 10 along the outer edges of the working electrode 20 and stack base 70. Details of the electrode stack assembly are explained below.

The reservoir is manufactured from a corrosion resistant engineering plastic such as a polysulfone or polycarbonate. The reservoir includes an enclosed space where electrolyte and a reservoir wick co-inhabit. The reservoir is not filled complete with the electrolyte, allowing free volume in the reservoir to allow for both water absorption, increasing the electrolyte volume, or water loss through evaporation past the working electrode, reducing electrolyte volume. The reservoir wick 80 uses capillary rise as the driving force to move the electrolyte out of the reservoir and into contact with the working electrode 20, reference electrode 50 and counter electrode 60. Electrolyte diffuses through separator disks shown and referred to generally as 40. Specific separator disks are labelled 41, 42 and 43.

The top of the reservoir 90 is a solid base that supports the electrode stack assembly 100. The first component of the electrode stack assembly 100 is the stack base 70 which lays directly on top of the reservoir and the reservoir wick, with the electrolyte on the reservoir wick 80 touching separator disk 43 through the hole in the stack base 70, allowing access of electrolyte to the separator disk 43. Separator disk 43 has a larger diameter than the stack base hole but has a smaller or equivalent diameter to the largest dimension of the counter electrode 60, as shown in Figure 2. Platinum strips, shown as 31, 32 33 is an electrical conductor, connecting the counter electrode 60 to the terminal pins in the sensor housing (not shown). Electrolyte reaches the bottom separator disk 43 by contact with the reservoir wick 80; likewise, electrolyte is transported around counter electrode 60 on to the next separator disk 42 by intimate contact of the two separator disks 42 and 43 outside the edges of the strip designed counter electrode 60; however, the particular way in which the counter electrode is configured is important to the invention and is discussed further below. The reference electrode 50 is usually oriented with the electrode support on the bottom and the catalytic material facing upwards, towards the working electrode 20. The reference electrode 50 has a smaller diameter than the separator disks 41 and 42 so that the two disks, sandwiching on both sides of the reference electrode 50 are in

intimate contact at their periphery to allow electrolyte transport around the outside of reference electrode 50. Another platinum strip 31 is then placed across the top of the reference electrode 50 to make electrical contact with a second terminal pin which is part of the sensor housing (not shown). The top separator disk 40 contacts directly the working electrode catalyst on the working electrode 20 at the top of the stack. The third platinum strip 31, connecting to the third terminal pin in the sensor housing (not shown) is laid across the top of the separator disk before the working electrode 20 is located. The working electrode 20 is located face down with the gas porous support facing upwards, in direct contact with the ambient air under test. Finally, 'O' Ring 10 is laid on top of the electrode stack assembly 100 and the top half of the sensor housing (not shown) compresses the 'O' Ring 10. The 'O' ring 10 presses on to the reservoir base, trapping the working electrode 20 and stack base 70 components, creating a seal since the reference electrode 50, counter electrode 60 and separator disks 40 are all inside inner diameter of the 'O' Ring 10, shown as D_{in} in Figure 1.

The electrode stack assembly 100 further comprises the working electrode 20, which contains the catalyst that oxidises or reduces the target gas. This electrochemical reaction produces an electrical current which is conducted via a platinum strip 31 to outside of the electrode stack assembly 100, leading to a current measuring circuit to determine the current produced by the oxidation or reduction of the target gas. Preferentially the catalyst operates selectively, oxidising or reducing the target gas whilst not electrochemically reacting with other gases in the sampled atmosphere.

This critical reaction at the working electrode requires ion transport between the working electrode and the counter electrode. In this invention, this is accomplished using liquid or gel electrolyte immobilised on wicking material, although solid state ion exchange systems, for example sulfonated PTFE such as Nafion®, would also benefit this invention. Capillary rise, the electrolyte transport driving force, ensures adequate electrolyte at the catalyst surfaces since the reactions at the working electrode will generate and or consume ions that must be either replenished or transported away from the working electrode surface to maintain the steady state required for correct operation.

Electrolyte transport occurs in the present invention by the stack of separator disks 41, 42 and 43 which touch each other on the top and bottom surfaces, near the periphery of the disk, outside of the edge of the counter electrode 60 and reference electrode 50, as taught by Shaw in US patent 3,755,125 and function as electrolyte transport means. As discussed below, and unlike Shaw, the separator disks 40 do not touch each other around the full perimeter of the counter electrode 60. The separator disks 40 are replenished with electrolyte from the partially filled reservoir 90 using wicking through the reservoir wick 80. The reservoir wick 80 is in intimate contact with the first separator disk 40 by the hole in the stack base 70. The stack base 70 is manufactured from gas porous hydrophobic polymer; examples of such material are Zytex® and Goretex®.

Electrolyte is forced by capillary action ("wicking") to provide a continuous path for ionic transport between the catalyst on the working electrode, the catalyst on the counter electrode and (optionally) the catalyst of the reference electrode. Continuous capillary action is maintained by the use of hydrophilic non-conductive planar disks interposed between the electrodes and since their diameter is greater than the electrodes, they touch outside of the electrodes. These hydrophilic planar electrodes are in intimate contact with a reservoir, which is partially filled with electrolyte,

1 and may include hydrophilic non-conductive filter material to provide a continuous electrolyte path from the reservoir
2 to the planar hydrophilic disks. Diffusion may be by either Fickian or Knudsen gas diffusion.

3
4 The counter electrode responds to the electrical demands of the working electrode. The counter electrode must either
5 reduce or oxidise a locally available electroactive chemical species such as protons or oxygen molecules; this counter
6 electrode reaction is the opposite sense of the working electrode: oxidation at the working electrode demands
7 reduction at the counter electrode. In a carbon monoxide sensor it is commonly believed that the reaction on the
8 counter electrode is the reduction of oxygen, typically balancing an oxidation reaction on the working electrode, such
9 as the oxidation of carbon monoxide.

10
11 The preferred embodiment described in Figure 2 also includes a reference electrode 50, which has not yet been
12 discussed. The reference electrode 50 provides a standard voltage which, in a potentiostatic circuit, sets the working
13 electrode operating potential. This ensures that the electrochemical reaction of the working electrode is the preferred
14 reaction. Referring to Figure 2, the reference electrode 50 is isolated from the stack base 70 and working electrode
15 20. The reference electrode is surrounded by separator disks 41 and 42 to ensure adequate supply of electrolyte to
16 either side of the reference electrode.

17
18 Preferably the reference electrode contains a catalyst in combination with a binder such as PTFE. This porous
19 binder/catalyst electrode is then bonded to a hydrophobic or hydrophilic support. In the preferred embodiment the
20 support is a hydrophobic PTFE material, either solid or gas porous. In the preferred embodiment the reference
21 electrode 50 is surrounded by two hydrophilic separator disks 41 and 42 coated with electrolyte. This design reduces
22 the availability of oxygen to the reference electrode 50; this is usually not a problem since the reference electrode
23 generates very little current and hence the dissolved oxygen available in the electrolyte is normally adequate to
24 maintain the redox couple at the reference electrode.

25
26 Part of the counter electrode 60 reaches to either the edge of the separator disk or just beyond. This ensures that when
27 the O-ring compresses the electrode stack assembly then the working electrode 20 and stack base 70 are in intimate
28 contact with the periphery of the top and bottom of the counter electrode. The counter electrode 60, on a gas-porous
29 substrate, will be trapped between items 20 and 70, allowing oxygen to flow through the gas porous support 21 of the
30 working electrode 20 and either directly to the edge of the counter electrode 60 or to the stack base 70 which then
31 contacts the counter electrode 60 from below. This two way access from the top surface of oxygen to the counter
32 electrode 60 allows adequate oxygen to balance the current generated the working electrode at extremely high
33 currents; an example would be 1% CO in emissions monitoring.

34
35 Figures 5 and 6 show the electrode stack assembly 100 in two different cross-sections. In Figure 5, the perimeter of
36 the counter electrode 60 is enclosed by the edges of the separator disks 40, allowing electrolyte to pass around the
37 counter electrode 60 for replenishment from the reservoir 90. However, in a different cross-section shown in Figure
38 6, the counter electrode 60 extends around the separator disks 40 allowing it to contact the working electrode support
39 and separator disks, thereby allowing oxygen to diffuse to the counter electrode. Figures 5 and 6 show the working
40 electrode 20 comprising a hydrophobic gas porous support 21 with catalyst 22 thereon. Correspondingly, the counter

electrode 60 comprises a hydrophobic gas porous support 61 with catalyst 62 thereon and the reference electrode comprises a hydrophobic gas porous support 51 with catalyst 52 thereon.

This aspect of the invention can be seen as provision of a gas diffusion means, comprising the stack base 70 and the gas porous support 21 of the working electrode, with which the counter electrode 60 is in contact around part of its edge whilst part of the counter electrode 60 is not in contact with the gas diffusion means and so provides a gap through which electrolyte can pass. The essential property of the gas diffusion means is that it provides a good gas diffusion pathway, being essentially free of electrolyte, to the counter electrode 60.

The main gas diffusion pathways are shown in Figure 4. Pathway 200 is slow, as the reagent gas for the counter electrode needs to diffuse through the electrolyte. This is analogous to the classical diffusion pathway found in Shaw and Binder. Pathway 210 illustrates diffusion of residual air volume from the reservoir 90 to the counter electrode and is previously known. Pathway 220 shows diffusion to the counter electrode through the gas diffusion means as envisaged in the present invention which combines this diffusion pathway with supply of electrolyte around the counter electrode 60. Pathway 230 is an additional diffusion route under the 'O' ring 10.

Alternative embodiments are shown in Figures 2 and 3. In one alternative embodiment the reference electrode may be a strip 53 extending to a diameter less than the O-ring 10 inner diameter but contacting the working electrode 20 analogously to the design of the counter electrode in order to allow flow of oxygen to the reference electrode. It may be that the preferred reference electrode has direct access to the gases available in the ambient air. For example, if hydrogen is readily available in the air under test then, through the same route as oxygen to the counter electrode, hydrogen could get to the reference electrode changing the preferred chemistry and modifying the electrochemical performance of the sensor: see UK patent application no. GB0011511.

In a further embodiment the counter electrode can be a disk 63. The preferred embodiment 60 increases the flow of oxygen to the counter electrode but performance advantages can be gained by reducing the oxygen access to the counter electrode, forcing it to use other electrochemical species such as protons. This could be accomplished by making the counter electrode as a disk 63 so it is not in direct contact with the working electrode 20 or stack base 70. In addition an annular separator disk from solid (i.e. not gas porous) material with the same geometry as the stack base 70 would reduce oxygen dissolution into the electrolyte. In other words one practised in the art can use a combination of solid polymer barriers and gas porous electrode stack supports to reduce oxygen access.

In a further embodiment the counter electrode strip 64 is narrower at the periphery with a large circular area in the centre in order to optimise the wicking area. In electrochemical gas sensors where the performance may be improved by increased counter electrode area this geometry will show certain advantages, although it may be more expensive to manufacture.

In a further embodiment it may be economical to manufacture a single electrode and then cut this into two components: one half of this electrode can be used as reference electrode 54 and the other as the counter electrode 63,

1 with the peripheral planar surfaces of both electrodes having intimate access with the gas p r us surfaces of the
2 working electrode 20 and stack base 70. Reference electrode 54 and counter electrode 65
3 need not be exactly one half the diameter: it may be advantageous if the electrodes are not fully semicircular or have
4 a reduced 90 degree radius. The advantage of this embodiment is a lower cost of electrode manufacture.

5
6 In a further embodiment the counter electrode is in the shape of a cross, as shown in item 66 in Figure 3. This
7 alternative counter electrode design maximises oxygen flux to the counter electrode 66 for reactions at very high gas
8 concentration applications, such flue gas emission monitoring.

9
10 In a further embodiment the reference and counter electrodes can be combined onto the same substrate, as has been
11 taught by Tataria (US patent 4,84,937 figure 3). Advantages include lower cost and simplifying the number of
12 components in the electrode stack assembly, eliminating the reference electrode platinum strip 32, reference electrode
13 50 and the separator disk 42 between the counter and reference electrodes. The simplicity of design produces the
14 lowest cost sensor and may be adequate where certain performance criteria are not critical.

15
16 The various embodiments of the reference electrode 50 53 54 and counter electrode 60 62 63 64 65 may be used in
17 different combinations, although it is not preferred to use both a disk counter electrode 63 and disk reference
18 electrode 50.

19
20 In a further embodiment the counter electrode may be turned upside down so that the support is next to the stack base
21 70 and the catalyst and binder face towards the reference electrode 50. This eliminates the need for the bottom
22 separator disk 43. The choice of counter electrode orientation depends on the ability to manufacture reliably and any
23 electrochemical advantages arising from the alternative counter electrode geometry.

24
25 There is an additional design parameter which is important when supplying a chemical source to the counter electrode
26 to ensure a stable electrochemical sensor. In a three-electrode system, with potentiostatic control, if the counter
27 electrode does not have adequate oxygen then the counter electrode potential will change, looking for the next species
28 to reduce. In a typical gas sensor design protons are available from the electrolyte (such as sulphuric or phosphoric
29 acid) to provide the necessary reactants for the counter electrode. So it is predicted and observed that when available
30 oxygen is depleted in typical electrochemical gas cells the counter electrode will next reduce hydrogen protons,
31 generating hydrogen gas. This will allow the sensor to continue to generate the required counter current, but the by-
32 product of hydrogen gas inside of the electrochemical sensor may change the performance of the sensor; this may be a
33 disadvantage to avoid or an enhancement to encourage.

34
35 In a further embodiment the reference electrode is disk shaped, and with a solid, non gas permeable polymer support:
36 this solid support reduces the diffusion of any gases generated by the counter electrode, such as hydrogen gas. In this
37 context non-gas permeable means sufficiently low permeability that gas diffusion is predominantly Fickian. This
38 shielding of the reference electrode by the support can be enhanced by adding a metal or metal-organic layer which
39 absorbs hydrogen or any other unwanted gas; this layer acts as a buffer to mitigate unwanted surges of hydrogen gas
40 when the sensor is exposed to high gas concentrations.

1
2 Although the preferred embodiment is configured to allow direct contact between the counter electrode 60 and the gas
3 diffusion means, a variant is envisaged where there is not direct contact. Oxygen can also get to the counter electrode
4 by diffusion of oxygen through the sulphuric acid analogous to gas flow in the Patent of Shaw 3,755,125. Diffusion
5 is very slow through sulphuric acid; however, the provision of the gas diffusion means allows good gas diffusion
6 close to the counter electrode and a short distance, such as 0.5 to 1mm of diffusion through sulphuric acid may be
7 acceptable in some variants where the counter electrode reaction current is small.

8
9 In a further embodiment an additional gas porous or solid annulus may be added to increase the stiffness of the
10 electrode stack assembly; this would also require additional separator disks 40.

11
12 Further modifications and improvements may be made by one skilled in the art within the scope of the invention
13 herein disclosed.

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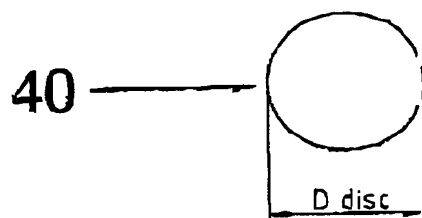
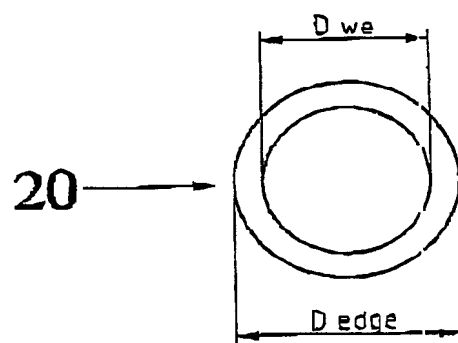
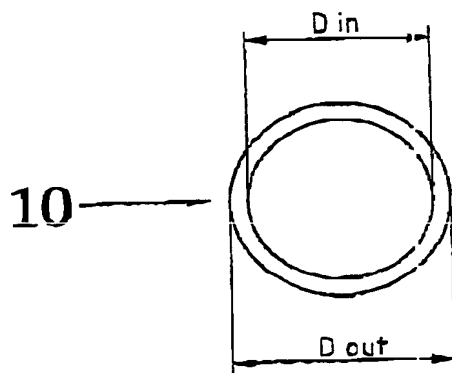


FIGURE 1

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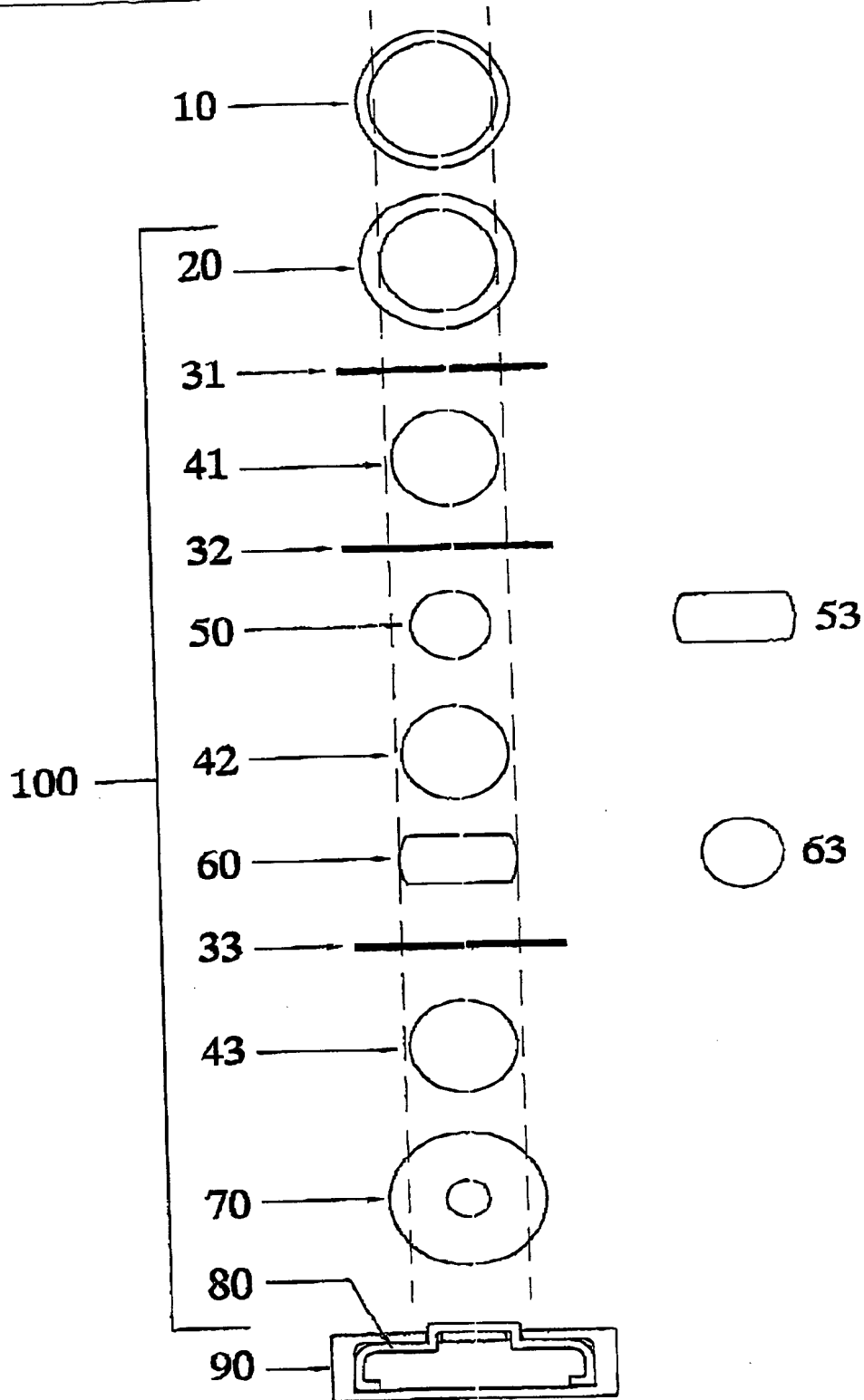


FIGURE 2



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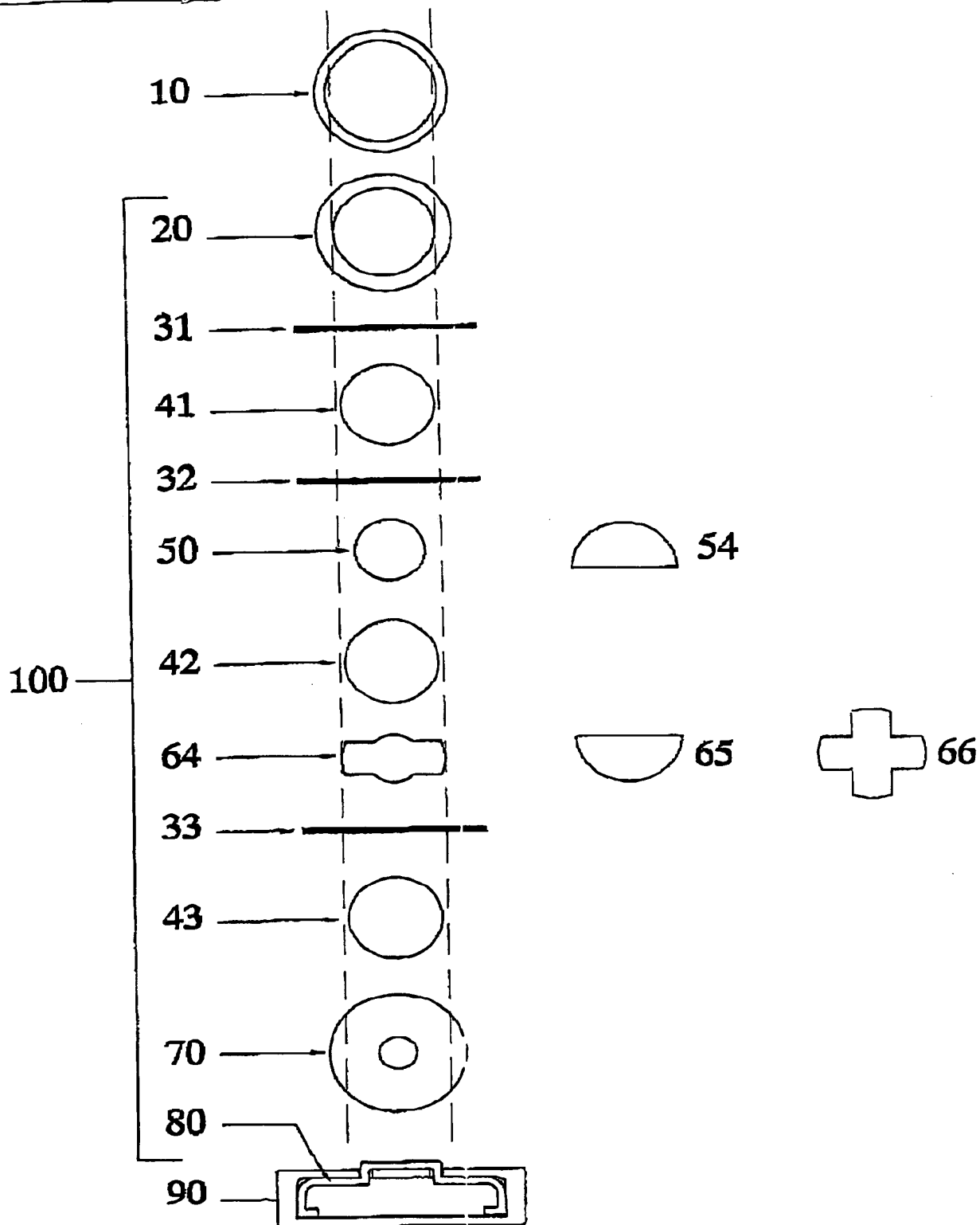


FIGURE 3



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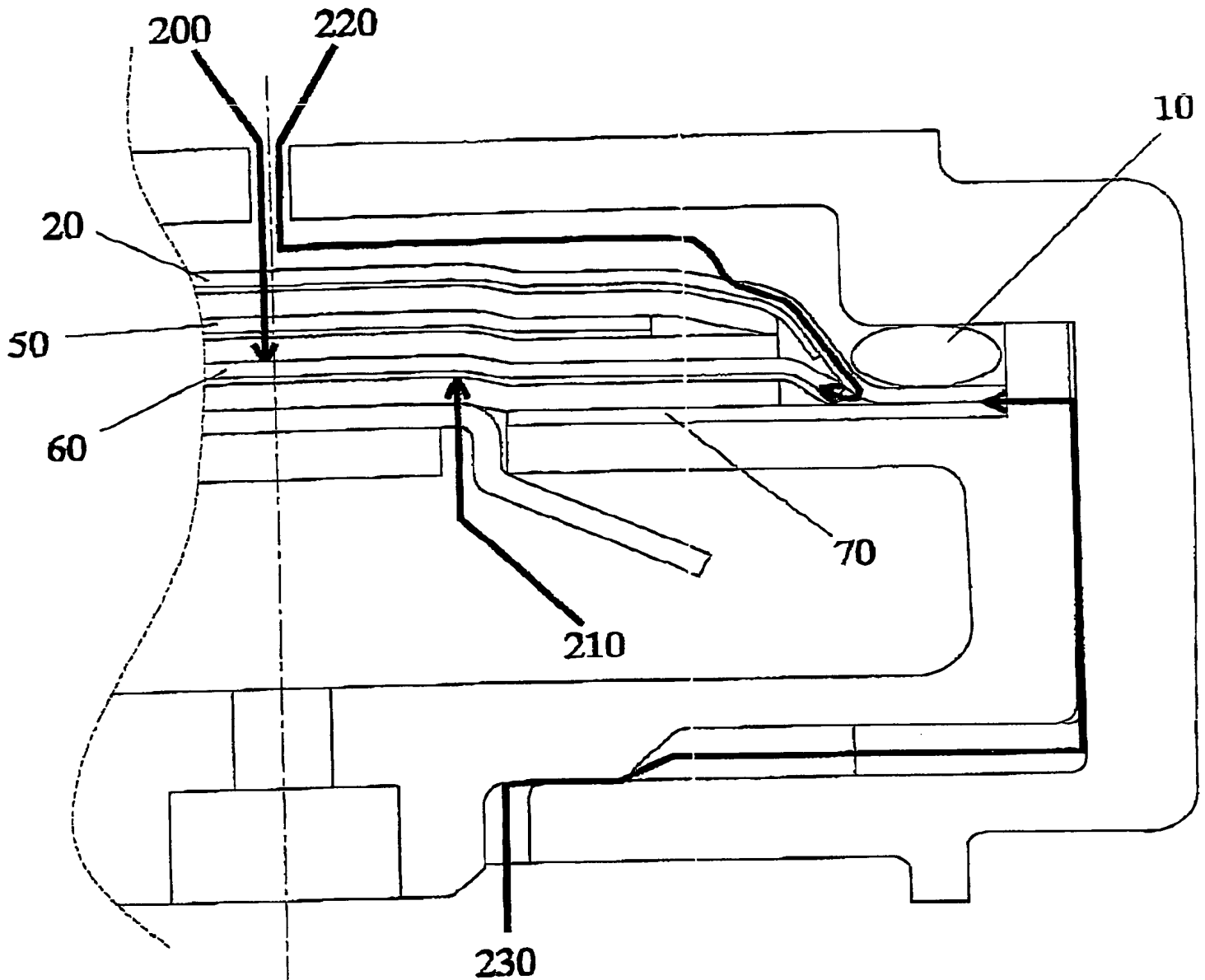


FIGURE 4

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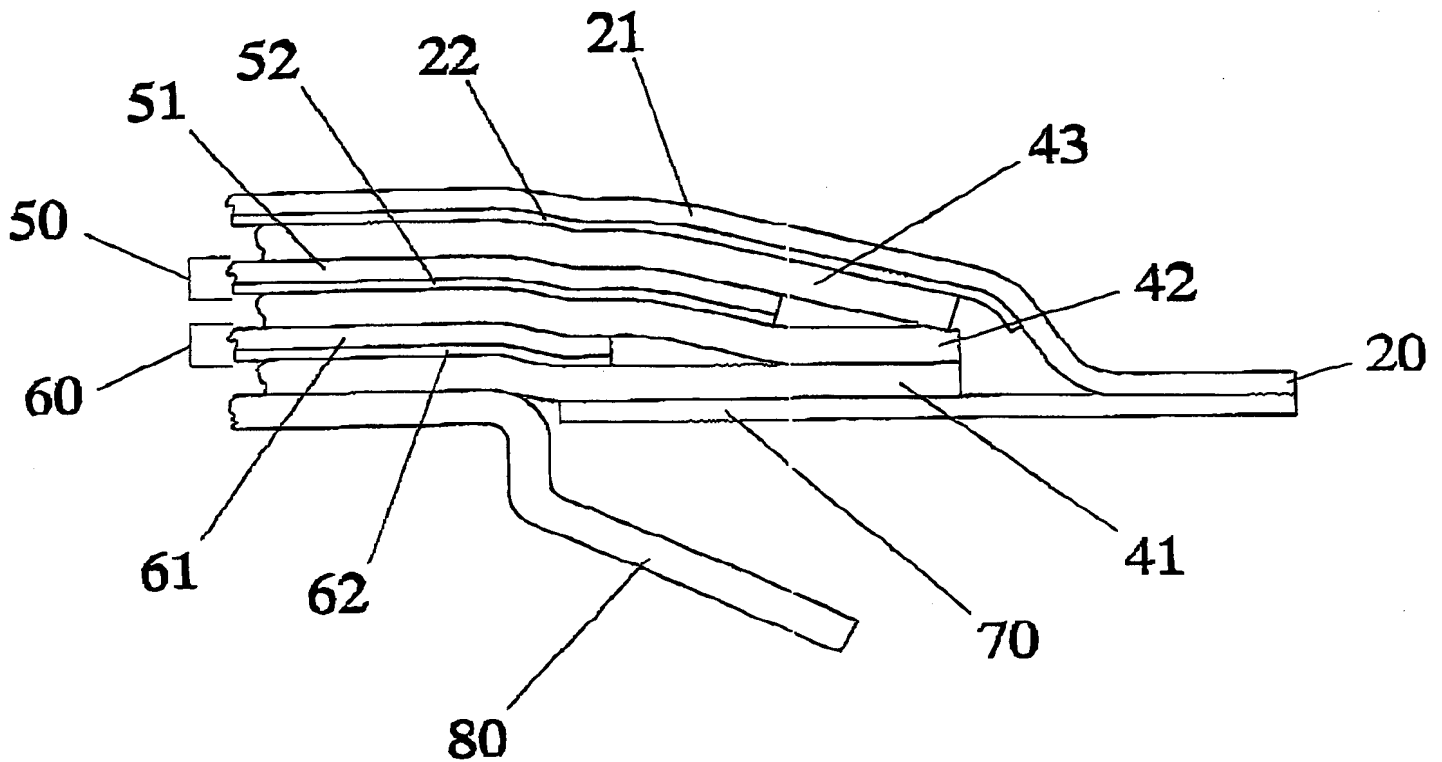


FIGURE 5



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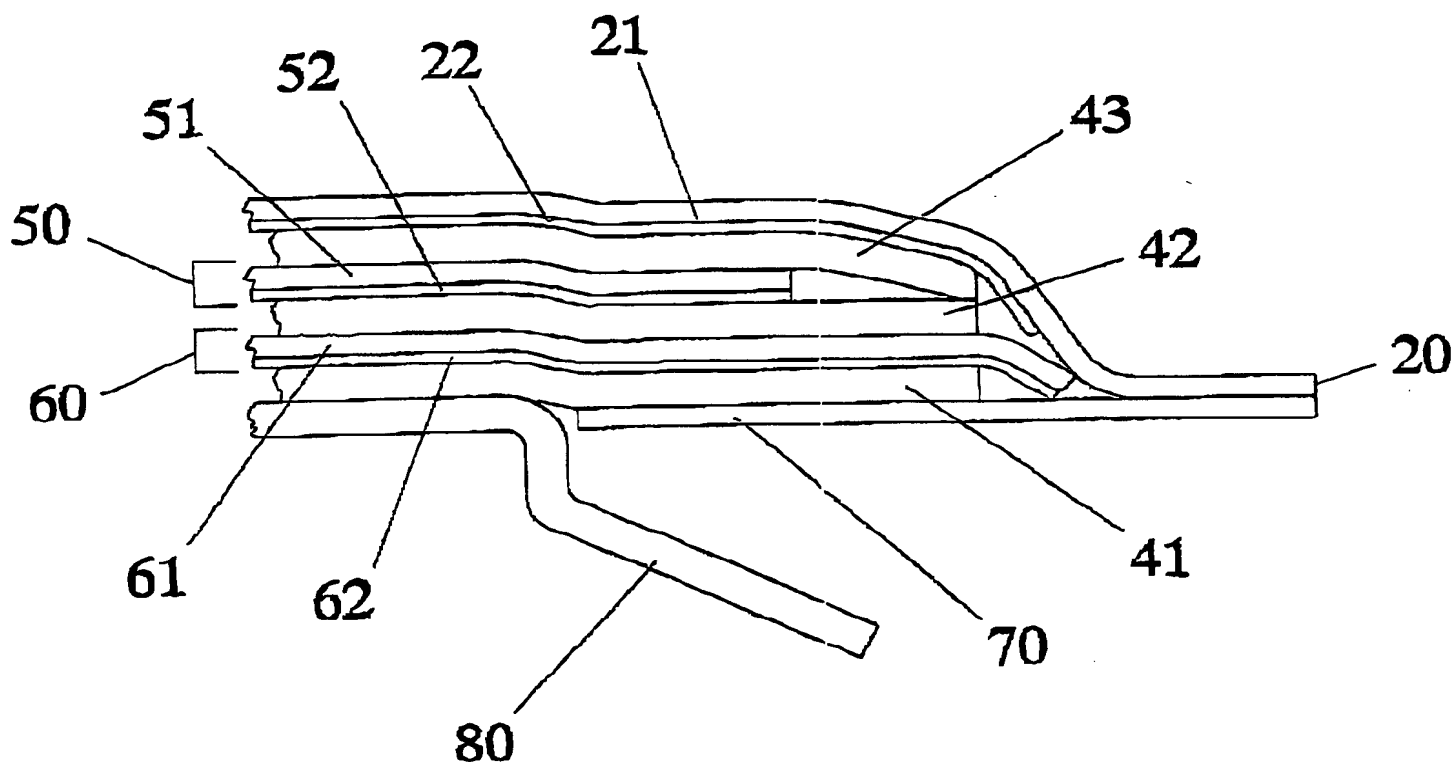


FIGURE 6

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